Paper No. 32

EVALUATION OF RADIOISOTOPE TRACER AND ACTIVATION ANALYSIS TECHNIQUES FOR CONTAMINATION MONITORING IN SPACE ENVIRONMENT SIMULATION CHAMBERS*

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ABSTRACT

The use of radioisotope tracer and activation analysis techniques in the determination of space simulation chamber contaminant levels was evaluated in a theoretical study. Each procedure was evaluated based on its sensitivity, ability to identify specific contaminants, speed of analysis, suitability for real-time operation, radiological safety and cost of implementation. Of the many techniques considered, only alpha particle range variation with mass density of chamber atmosphere, indicated a sensitivity, 1.9×10^{-10} g/cm^2, competitive with methods presently in use.

INTRODUCTION

The objective of this study was to determine the feasibility of several nuclear analytical techniques for the identification and measurement of very small quantities of contaminants in space environment simulation chambers at NASA Manned Spacecraft Center. This project was carried out in two phases: Phase I being directed toward the use of radioactive isotope techniques while Phase II was concerned with the use of activation analysis. The merits of a given technique are evaluated on the basis of measurement sensitivity, ability to identify specific contaminants, speed of analysis, suitability for real-time operation either in-chamber or on-site near the chamber, radiological safety and cost of implementation.

PRESENT METHOD SENSITIVITIES

For purposes of comparison the maximum sensitivity as quoted in the literature for methods presently in use was chosen as the design objective. For the Contamination Control Units (CCU) system (1) and for the Quartz Crystal Microbalance (QCM) system (2) this limit is 10^{-9} g/cm^2. This design basis sensitivity is somewhat artificial as the typical contamination levels during chamber tests have been reported to be 1×10^{-7} g/cm^2(3).

RADIOISOTOPE TAGGING

General--Two methods were considered for tagging the suspect
molecules with a radioactive atom; isotopic exchange with a high
specific activity isotope and transmutation by neutron irradia-
tion. The former requires a high specific activity source of the
element of interest to be mixed with the suspect agent and chem-
ical exchange between radioactive and non-radioactive atoms to
occur. This is generally performed with small quantities of
materials and the extent of tagging which occurs varies greatly
among compounds. The latter technique is essentially that of
producing a radioisotope by neutron activation, the amount pro-
duced depending on the neutron flux intensity and the time of
irradiation. One problem with this technique is that of radia-
tion damage to the molecular structure of the compound thus
changing its chemical properties. Obviously an irradiation time
must be chosen which is a compromise between sufficient activity
and minimum radiation damage.

Major Composition Elements--The majority of the suspect agents
can be described as hydrocarbons many of which incorporate sili-
con in their structure. In the calculations which follow Dow
Corning 704 vacuum oil, DC 704, was considered as a typical
agent. For tagging of carbon or hydrogen only isotopic exchange
is feasible and the radioisotopes ^{14}C and ^{3}H were considered
respectively. As both isotopes decay by low energy beta emission
and have rather long half lives, several constraints are imposed
on the detector system and by radiological safety considerations
on the usage of the method. The isotopic tag was calculated
based on exposure of one gram of the suspect agent with the
source and achieving a specific activity of 1 millicurie/gm (4).
This small amount was then distributed throughout the total sus-
pect agent volume and a final molecular tagging efficiency of
$7 \times 10^{-8}\%$ was assumed.

    The silicon tag was obtained by the neutron activation
technique which for the purposes of these calculations assumed
the following: neutron flux of 5×10^{12} n/cm^2/sec, one hour ir-
radiation, DC 704 oil with three silicon atoms per molecule, and
incorporation of the radioactive agent in the vacuum system one
hour after the end of irradiation. The tagging process converts
stable silicon-30 to ^{31}Si which has a 2.6 hour decay half life.

    The detector system considered had to be able to measure
the low energy betas, 18 KeV, emitted by ^{3}H as well as the
higher energy radiation emitted. Among the systems considered
were high pressure gas detectors, avalanche detectors, scintilla-
tion detectors and semiconductor detectors. The optimum system
design was exhibited by a large surface area, radiantly-cooled
plastic scintillator which had the desirable properties of no
detector window absorption, large sensitive volume, and minimal

expense.

The resulting analysis yielded the following detectable amounts of DC 704:

$$^{14}C \text{ tag } - 1.3 \times 10^{-4} \text{ g/cm}^2$$
$$^{3}H \text{ tag } - 2.7 \times 10^{-7} \text{ g/cm}^2$$
$$^{31}Si \text{ tag } - 2.7 \times 10^{-5} \text{ g/cm}^2$$

Obviously the ^{14}C and ^{31}Si tag sensitivities are inadequate and the ^{3}H tag is marginal at best. The radiological safety complications posed by the 12.33 year half life (5) of the ^{3}H would probably negate its use. However if the tagging efficiency could be increased by a factor of 100, the sensitivity is correspondingly lowered to 2.7×10^{-9} g/cm^3 which becomes competitive with other techniques.

Minor Composition Element--Analysis of several oil samples indicated the presence of trace amounts of sodium (Na) and bromine (Br). Following the procedure outlined for the silicon tagging, the detectable limits for various oils were calculated based on transmutation of the Br and Na impurities into a radioactive tag. The values calculated for the detectable limits were in the range of 3×10^{-3} g/cm^2 for Na and 3×10^{-4} g/cm^2 for Br. Thus the use of the trace impurities as a tagging procedure was quite unacceptable.

NON-RADIOACTIVE ISOTOPE TECHNIQUES

Consideration was also given to using stable isotopes, namely carbon-13 and deuterium as a means of tagging a particular oil followed by a subsequent analysis by Nuclear Magnetic Resonance (NMR) or Mass Spectrometry. The rather large sample size required, 1 to 10 mg, and the percentage tag required in order to obtain sufficient sensitivity precluded further consideration of this approach.

CHARGED PARTICLE RANGE

General--The monoenergic nature of heavy charged particle emission and the single valued limited magnitude nature of subsequent range led to the consideration of this method for gross contamination monitoring. The general design for the system consisted of a source with two tubes extending out from it, a variable absorber, and two detector systems placed one each at the ends of the two long tubes, opposite the source (Figure 1). Both detectors are movable and track evenly. One tube is open to the atmosphere of the chamber, whereas, the other tube, filled with clean air, is sealed and a check valve-bellows system for pressure equalization with the chamber. With the detectors positioned at the point of maximum variation of range

with incremental abosrber thickness, the difference in count rates between the two detector systems allows determination of contamination in the chamber.

Fission Fragment Range--The consideration of fission fragments violates the previously assumed monoenergic property however these high mass, high energy charged particles have a very short range. A typical curve of intensity, $I(X)$, vs range, X, and $dI(X)/dX$ vs X are given in Figure 2. The range value used for the calculation was that which resulted in the steepest slope of dI/dX i.e. ~ 0.97 of XMAX. Assuming a counting precision of 0.1%, a detection sensitivity of 2.3×10^{-6} g/cm^2 resulted.

Alpha Range--The typical intensity vs range characteristics for alpha particles are illustrated in Figure 3. The only significant difference between this analysis and the previous one for fission fragments is the larger values of dI/dX obtained due to the monoenergic nature of the particles. This results in a detection limit of 1.9×10^{-10} g/cm^2 which is quite competitive with existing techniques of impurity analysis.

The method is particularly unique in that it actually measures total mass between the detector and the source, thus responding to condensable and non-condensable contaminants. Assuming a ten meter long tube, values as low as 2×10^{-13} g/cm^3 could possibly be detected.

SUMMARY OF ISOTOPE MEASUREMENTS

Of the isotopic methods surveyed in this analysis, only that of variation of alpha particle range with mass of the absorber is shown to have the sensitivity required to be truly competitive with the existing methods. The pertinent information on each technique considered is reviewed in Table 1.

NEUTRON ACTIVATION ANALYSIS

General--The feasibility of using neutron activation analysis to identify and locate sources of contamination in the NASA space environmental simulation chambers was also investigated. Several activation analysis alternatives were studied on the basis of technical feasibility, expected performance and cost. Efforts were directed primarily at the detection of several oils, greases, and paint which were suspected as likely contaminants. Charged particle and high-energy photon activation analysis techniques were not considered due to the high cost of particle accelerators and the lack of detailed experimental data on which to base sensitivity estimates.

The basic approach using neutron activation analysis involved detecting a specific element or set of elements whose presence in a sample uniquely identified a given contaminant

and whose concentration in a sample is directly proportional to the amount of that contaminant present. Since activation analysis is an elemental method, not capable of determining compounds or molecular structure, this approach requires that the elemental compostion of each possible contaminant contain a unique set of elements suitable for neutron activation analysis. This unique "fingerprint" characteristic may be an inherent pro-perty of the material or may be the result of a process in which certain suitable elements are placed into the compound for use as "tag" elements.

This investigation focused on the following six materials commonly used in the space environmental simulation chamber and which were thought to be likely contaminants:

>   Dow Corning 705
>   Dow Corning 11
>   Sun Vis 706
>   3-M Black Velvet Paint
>   Houghton Safe 1020
>   Houghton Safe 1055

Basic Description of the Method--Neutron activation analysis can be generally described as having three basic steps:

>   1.   sample activation
>   2.   sample cooling
>   3.   gamma ray spectrometry

Sample activation consists of irradiating a material with a flux of neutrons to produce radioisotopes by means of nuclear transmu-tation. Sample cooling is an optional step which may be used to allow undesirable short lived radioisotopes to decay to an ac-ceptable activity level before attempting to measure the activi-ties of the elements of interest. After suitable cooling period, gamma ray spectrometry is used to measure the energies and inten-sities of the various gamma rays emitted by the activated materi-al. Using the spectral data, a comparison can be made between the spectra from an unknown sample and those from a known stan-dard to provide identification of elemental constituents and a determination of the elemental concentrations. Under optimum conditions with high neutron flux densities, over half of the naturally ocurring elements can be detected in quantities below one microgram (6).

Activation Analysis of Potential Contaminants--Samples of the six potential contaminants were evaluated on the basis of their elemental composition to determine their suitability for detec-tion and identification using neutron activation. The major ele-ments comprising these materials include carbon, hydrogen, oxygen, silicon and phosphorus, none of which activate appreciably with thermal neutrons and only silicon, oxygen and phosphorus activate well with fast neutrons. Fast neutron activation analysis was considered as a possible technique but rejected due to lack of a

practical means of producing very high fluxes of fast neutrons required for sub-microgram measurement sensitivities. Since their major elements could not be used for "fingerprinting" the potential contaminants, analyses were carried out on samples of these materials to determine if minor or trace elements suitable for thermal neutron activation were present. Analyses were performed with a nuclear reactor which produces a usable thermal neutron flux of 5×10^{12} $n/cm^2/sec$. Gamma ray spectrometry was accomplished with a Ge(Li) detector and a 4096 channel pulse height analyzer. Results of these analyses, shown on Table 2 revealed no "fingerprint" elements in these samples which would be sufficiently reliable and unambiguous for use in contaminant identification. While several samples showed possible unique trace element patterns, such as hafnium in Houghton Safe 1020 and tungsten in Sun Vis 706, the low concentrations (sub-ppm) make detection of microgram amounts of samples virtually impossible by neutron activation analysis.

Inactive Tracers--When a material is inherently free of suitable "fingerprint" elements, it is sometimes possible to label or tag the material with an element or set of elements which can be measured with good sensitivity and specificity. This method of inactive or stable tracers offers many of the advantages of radioactive tracers while avoiding the radiological safety and radioactive contamination problems. Tagged materials would be used in the chamber in place of usual materials. Samples of contaminants would then be collected in the test chamber and analyzed by neutron activation to determine the identity and amount of each tag element present.

The sensitivity of this procedure for detecting small quantities of a tag element depends upon the element's activation cross section as well as the energy and intensity of the irradiating neutron flux. Reactor thermal neutron activation analysis provides a median detection limit of approximately 10^{-8} grams (6) whereas 14 MeV NAA provides a median detection limit in the range of 10^{-3} to 10^{-4} grams using a state-of-the-art Cockcroft-Walton type neutron generator (flux of approximately 2×10^8 $n/cm^2/sec$). It is obvious that for thermal neutron activation, elements with the best sensitivity (Eu, Dy, Mn, etc.) would be desirable for use as tags, however, a further requirement is that the tag element be chemically suitable for inclusion in the compound being labeled.

In view of this chemical compatibility requirement, a brief study was undertaken to determine the practicality and reliability of an elemental tagging system. In reference to the chemical makeup of the expected contaminant materials, a typical electrophilic aromatic substitution process (halogenation) was chosen for the tagging mechanics. The elements best suited for this tagging procedure and trace activation analysis are chlorine and bromine. The halogenation is expected to take place on the phenyl radical common to the proposed DC-11, DC-705, HS-1055,

and HS-1120 contamination materials. The general equation for this reaction is:

$$ARH + X_2 \xrightarrow{Lewis\ Acid} ARX + HX \text{ where:}$$
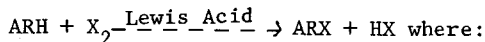
AR = phenyl radical
$X_2 = Cl_2$ or Br_2
Lewis Acid - $FeCl_3$, $AlCl_3$, etc.

Measurement Sensitivity--A primary measure of the effectiveness of a neutron activation analysis system for contaminant detection is the sensitivity with which tag elements can be determined under given conditions of sample acquisition, irradiation, and counting. A large number of variables must be considered in estimating measurement sensitivity, some of which are set by system design and others determined by the physical properties of the materials in the sample. The more important factors which influence system measurement sensitivity are:

1. Size of collected sample
2. Activation properties of tag element and other constituents in sample
3. Available neutron flux density
4. Irradiation time
5. Half-life of activation product
6. Delay between irradiation and counting
7. Detector background
8. Energy resolution of counting system

In order to assess the feasibility of using bromine, chlorine and iodine as tag elements to be detected by a neutron activation analysis system located in or near the chamber, a set of "best case" conditions were assumed and detection limits calculated. First, detection limits for elemental Br, Cl and I were calculated based upon a one hour irradiation with a thermal neutron flux of 1.25×10^9 n/cm^2/sec and counted with a 3 in. x 3 in. NaI(Tl) detector. Further assumptions which were made to determine "best case" performance are as follows:

1. Tag element is uniformly distributed in the contaminant material.
2. Only one contamination source is responsible for the tagged material deposited on the 3 inch diameter collection disk.
3. Tag element does not disassociate from the contaminant materials.
4. Average contaminant deposition is approximately 10^{-6} gm/cm^2.
5. A non-activable collection medium is used in lieu of presently used pyrex plate.

Assumptions one through three above are "best case" con-

ditions with respect to the measurement of trace element tags in chamber contaminant samples. To assure that the first three assumptions are valid would require further research beyond the scope of this project; however, it should be pointed out that variations in any one of these would significantly degrade the overall effectiveness of the tagging approach. Assumption number three (stability of tag element in the contaminant materials) is probably the most uncertain of all. The effects of extreme temperatures and high vacuum could cause the release of tag elements from the labeled material thus defeating the method. A quantitative evaluation of this factor would require extensive testing of various tagged contaminants under conditions equivalent to those present in the test chamber.

Four Irradiation Alternatives for Neutron Activation Analysis--
Four alternatives for a NAA system and their important characteristics are summarized in Table 3.

The on-line monitoring system proposed a shielded isotopic neutron source, sample changer, and a NaI(Tl) gamma ray spectrometer to be located inside NASA Chamber A. The major advantage of this type system is its ability to offer hourly real-time analysis during chamber operation. A major consideration in this approach would be the effect of hostile environmental conditions (ie. $125^{\circ}C$ and 10^{-6} Torr vacuum) inside the chamber during operation. Precautions must be taken to seal the shield assembly to prevent outgassing from the hydrogenous source shield.

The second alternative, a variation of the previous approach, involves the use of a subcritical multiplier system which employs a centrally located neutron source in a $233\text{-}U\text{-}H_2O$ or $235\text{-}U\text{-}H_2O$ solution. Such a system, as suggested by Currie, McCrosson and Parks (7), could enhance the neutron flux by factors of 6.4 and 4.8 respectively. However, to achieve these useful flux enhancement factors the assembly must be operated so near criticality that safety procedures and regulations may preclude practical application of this approach. Due to the complexity and size of this system, it would most likely be located outside the chamber, offering only daily analysis.

The third alternative, using a 14 MeV neutron generator as the source of neutrons was found to be unfeasible due to insufficient sensitivity.

The last technique proposed involved using the nuclear reactor at Texas A&M University. Although the return time analysis would be several days, the available thermal neutron flux of 4.3×10^{12} $n/cm^2/sec$ offers the best sensitivity and reliability for contaminant identification.

Summary of Neutron Activation Approach--While neutron activation analysis is well known as a highly sensitive trace analytical technique, it must also be recognized that ultimate sensitivities are achievable only under favorable conditions. This study has shown that conditions are very unfavorable for the on-site

detection and identification of microgram quantities of space
environmental chamber contaminants by neutron activation analysis
techniques. Factors supporting this conclusion are given below:

Lack of inherent contaminant "fingerprint":
Contaminant materials studied are composed of elements which do
not have suitable properties for neutron activation. Experimen-
tal results indicated no unique neutron activation products use-
ful for contaminant identification.

Contaminant tagging stability: Evaluation of chemical
stability of proposed tagged compounds under high vacuum and
temperature conditions would be required.

Neutron source replacement cost: Cf-252 (2.6 year half-
life) would require periodic replenishment at an average annual
cost of approximately 20 to 25% of the original source cost.

Reliability factor: Under "best case" conditions, the
expected performance of the in-chamber system can be rated only
marginal. Since the probability of achieving "best case" condi-
tions in actual test operations is unlikely, the in-chamber
system would not be a reliable solution.

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(7) "Neutron Sources and Applications", Proceedings of the American Nuclear Society, National Topical Meeting, CONF-710402 (Vol. 1) August 1971.

Table 1 - Summary of Isotopic Techniques

Method	Detection Limit g/cm^2	Advantages	Deficiencies
^{14}C	1.3×10^{-4}	Operational over complete system, allows selective testing of suspected agents on an individual basis.	Long half life radioactive contamination of chamber, tag may not follow more volatile fraction of compound.
^{3}H tag	2.7×10^{-7}	Operational over complete system, allows selective testing of suspected agents on an individual basis.	Long half life radioactive contamination of chamber, tag may not follow more volatile fraction of compound.
Na tag	1.7×10^{-3}	Selective tagging of some specific agents, operational over complete cycle.	Tag may not follow more volatile fraction of compound.
Br tag	2.9×10^{-4}		
^{31}Si tag	2.7×10^{-3}	Selective tagging of some specific agents, operational over complete cycle, also short half life isotope.	Severe time constraint on use of method, possible radiation damage to compound.
Alpha Range	1.9×10^{-10}	Fully operational over complete cycle, detects both condensable and non-condensable agents, system can be made very directional.	Size problems, sensitivity very directional dependent, new system never used before for this purpose.
Fission Product Range	2.3×10^{-6}	Same as alpha range.	Same as alpha range, also possible radioactive contamination problem.

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Table 2 - Elemental Analysis of Suspected Contaminants[1]

Sample / Element	Concentrations in ppm					
	Sun Vis 706	DC 705	DC 11	3m PT.II	HS 1020	HS 1055
Al[2]	25.0	537.0	1400.00	---	108.0	123.0
Br	0.49	0.52	---	39.0	5.0	1.8
Cl	28.0	15.0	35.0	52,000.0	118.0	313.0
Cu	2.8	0.32	13.0	0.64	1.2	0.47
I	1.9	---	---	---	---	---
La	---	0.08	---	---	---	0.06
Mn	---	---	0.90	---	---	---
Na	43.0	25.0	1106.0	20.0	50.0	25.0
V	0.19	---	0.63	---	---	---
W	0.11	---	---	---	---	---
Zn	168	---	2.4	2.7	1.3	---
Co	---	---	0.2	0.16	---	0.09
Hf	---	---	---	---	0.39	---

[1] Analyses performed using instrumental neutron activation
[2] Al data not corrected for Si interference due to $^{28}Si(n,p)^{28}Al$.

Table 3 - Summary of Irradiation System Characteristics

Technique	Initial Cost Analysis	Analysis Speed	Obtainable Thermal Neutron Flux[1] (n/cm^2-sec)	Measurement Sensitivity
On-line ^{252}Cf System (In-chamber)	$525,000[3]	Hourly	1.25×10^9	Poor
^{252}Cf and Multiplier System[2] (On-site)	$200,000[3,4]	Daily	1.52×10^9	Fair
14 MeV Generator (On-site)	$ 25,000	Daily	4.0×10^7	Very Poor
Reactor at Texas A&M University	$600 min.[5]	Several Days	4.3×10^{12}	Good

(1) Uniform flux over 3 inch diameter disk.
(2) 5-3 mg sources with a 4 times multiplier.
(3) Based on 10 dollars per microgram.
(4) Cost of multiplier approximately $50,000.
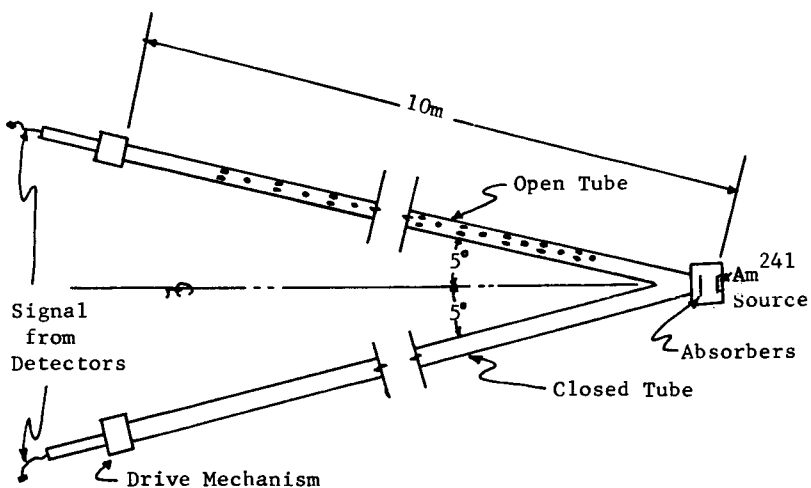(5) $300/day for reactor time plus $30/sample for analysis. Minimum 10 samples.

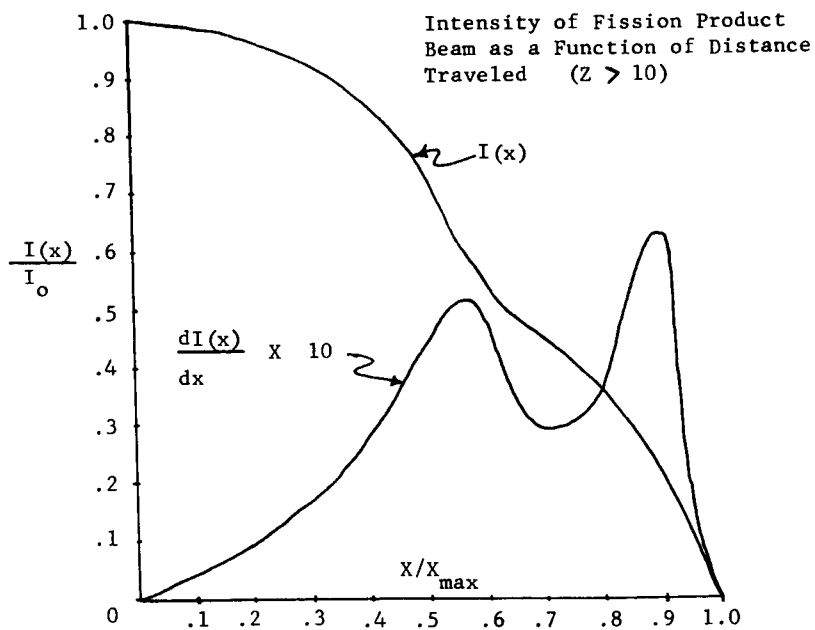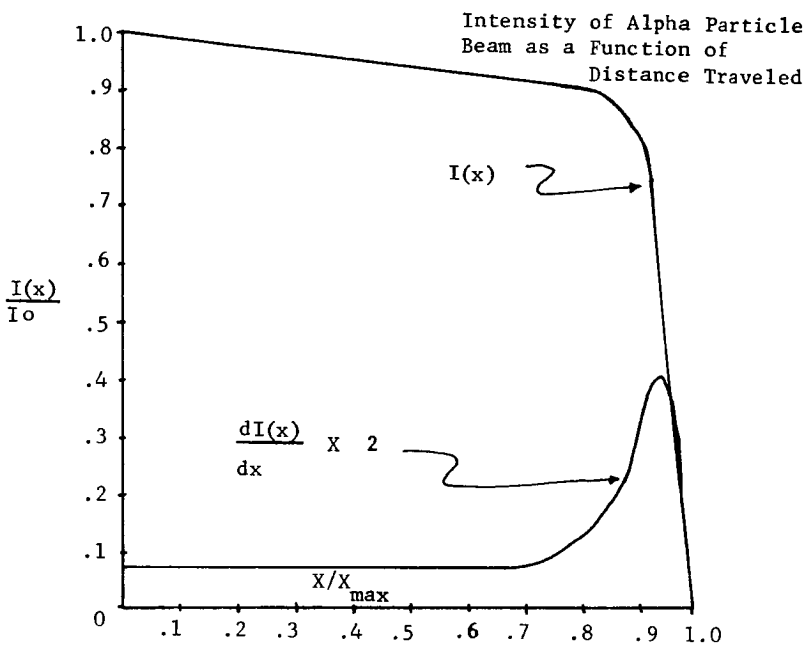Figure 1 - Charged Particle Range Equipment Layout.

Figure 2 - Fission Product Range Characteristics.

Figure 3 - Alpha Range Characteristics.